Chapter 1
Beginnings

Willst du ins Unendliche Schreiten,
Geh nur im Endlichen nach allen Seiten.
If you want to reach the infinite,
explore every aspect of the finite.
Johann Wolfgang von Goethe

1.1 Introduction

Thermodynamics is the science that first dealt with heat and the motion caused by heat. Initially that meant the conversion of heat into motive power using an engine and a working substance like steam. Such things were an integral part of the industrial revolution and the wealth of nations. But as the foundations of the science emerged it became clear that we were not dealing only with motive power. We were dealing with matter and energy at a very fundamental level.

Max Planck's use of thermodynamic entropy and his eventual acceptance of Ludwig Boltzmann's formulation of a statistical entropy led to the interpretation of the black body radiation spectrum and the birth of the quantum theory [94, 131]. Thermodynamic arguments were the basis of Albert Einstein's paper on Brownian motion that closed the arguments about the existence of atoms [48]. And Einstein's thermodynamic treatment of radiation in a cavity produced the photon [47, 94].

We will treat systems of atoms and molecules with the methods of statistical mechanics. This includes extreme situations such as high temperature plasmas and studies of the behavior of matter near absolute zero of thermodynamic temperature. The roots of statistical mechanics are in thermodynamics. And there remains a seamless connection between the two.

We will also study the foundations of the theory of chemical reactions. In the language of the chemist, the combination of thermodynamics and statistical mechanics is physical chemistry. And as the American chemist G.N. Lewis[1] once remarked, physical chemistry includes everything that is interesting.

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[1] Gilbert Newton Lewis (1875–1946) is one of the greatest of American scientists. He left an indelible mark on American teaching as well as research in physical chemistry.

C.S. Helrich, *Modern Thermodynamics with Statistical Mechanics*,
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For such a broad study we must carefully lay the foundations. And so we begin with heat and motion.

1.2 Heat and Motion

That motion can cause heat through friction is a part of common experience. To reverse the process and produce motion from heat required imagination and ingenuity. Then later it became evident that ingenuity alone did not suffice. A deeper understanding of matter and of energy was required. By the end of the 19th century this was beginning to crystallize as the sciences of thermodynamics and kinetic theory began to emerge.

That heat could cause motion occurred to people as they noticed the production of vast amounts of steam from the boiling of water. Hero (Heron) was a Greek mathematician (geometer) and writer on mechanics who lived in Alexandria in the first century of the common era. Among the known works of Hero is the record of an engine which used heat from a fire, and steam as an intermediary, to produce motion.

Hero's engine was a glass globe pivoted on glass tubes, which fed steam from a cauldron to the globe. The steam escaped through tubes located circumferentially around the globe. The tubes were bent so that the steam escaped tangentially and the globe rotated on its axis. This is a reaction engine. The force driving the engine was generated by the steam in the same sense as the thrust of a rocket engine is generated by the escaping gases. But the source of the motive power was the fire that produced the steam.

A steam pump developed by Thomas Savery in 1698 used heat to do work with steam as an intermediary. This pump was used to raise water for supplying reservoirs and in pumping water out of coal mines. Mines became flooded when excavation intersected ground water sources. A modification of Savery's pump, which actually included a cylinder, was produced by Thomas Newcomen in 1705. The action was slow and probably required the operator to manage the valves by hand. James Watt, an instrument maker in Glasgow, when employed to repair a Newcomen engine, observed that the action could be made more efficient. By 1782 Watt was producing an engine with a flywheel and continuous operation.

Much of the effort in steam engine development in the 18th century was of the sort of practical nature that required only a rudimentary concept of forces and a good dose of ingenuity. The engineer simply did not have the scientific tools necessary to design efficient engines.

At the beginning of the 19th century there were two competing concepts of heat, but really only one theory. One concept was that heat is a substance, referred to as caloric . The other concept was that heat is actually the motion of the constituents of matter. There was a theory for caloric; but there was no well-structured theory for the kinetic concept of heat. Therefore, even though some of the bases of the

caloric theory were refuted experimentally at the end of the 18th century, there was no competing theory providing an alternative.[2]

In 1824 a remarkable memoir *Reflexions sur la puissance motrice du feu et sur les machines propre à développer cette puissance,* usually translated simply as *Reflections on the motive power of fire*, was published by a young French military engineer, Sadi Carnot,[3] outlining the concepts of the motive power of heat [21].

Unfortunately Carnot's memoir, which was written in non-mathematical language so that practical engineers would find it accessible, was essentially ignored by both engineers and scientists until its republication by Émile Clapeyron[4] two years after Carnot's death.

In the memoir Carnot made three primary points: (1) heat engines work because caloric flows through them much as water flows over a water wheel, (2) an efficient heat engine should operate in a cycle, in which the working substance[5] remains enclosed in a cylinder fitted with a piston, and (3) the most efficient engine should be reversible in the sense that in each step there is a very small difference between the forces and temperatures within the cylinder of the engine and those outside [21]. Very small changes in external conditions could then reverse the direction of the process and the heat engine could operate as a heat pump, pumping the caloric upwards across the temperature difference as a water pump.

Carnot explicitly cited, with praise, the British and Scottish engineers who had invented and developed the steam engine [[55], p. 63]. But Carnot's ideas put to an end the implicit belief that efficient steam engines could be built on the basis of ingenuity alone. Carnot had presented a new concept in which the heat itself was the important quantity, not the force of the steam on the cylinder.

The diagram in Fig. 1.1 illustrates the Carnot idea. In Fig. 1.1 the heat engine is represented by a filled circle.

Theoretically caloric was a conserved quantity. So a continuous arrow of uniform width is used to represent the caloric flowing through the heat engine. Work is produced as the caloric falls through the temperature difference, so the arrow representing work is separate from the caloric arrow. Carnot showed that the efficiency of the engine, which is the work done divided by the caloric input, must be independent of the working substance in the engine and is a function only of the height of fall, i.e. temperature difference. He was, however, unable to obtain a functional form for the efficiency.

Carnot later rejected the caloric theory. But he published nothing after the memoir. We know of Carnot's rejection of the caloric theory from his scientific notes. These had been in his brother's possession for forty-six years after Carnot's death, and were finally published in 1878 [37].

In the notes Carnot writes "... we may state as a general proposition, that the quantity of motive power in nature is fixed and that, strictly speaking, motive power

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[2] These classic experiments are those of Benjamin Thompson (Count Rumford) and Humphry Davy.

[3] Nicolas Léonard Sadi Carnot (1796–1832) was a French physicist and military engineer.

[4] French engineer Benoît Paul Émile Clapeyron (1799–1864).

[5] Carnot used air in his example.

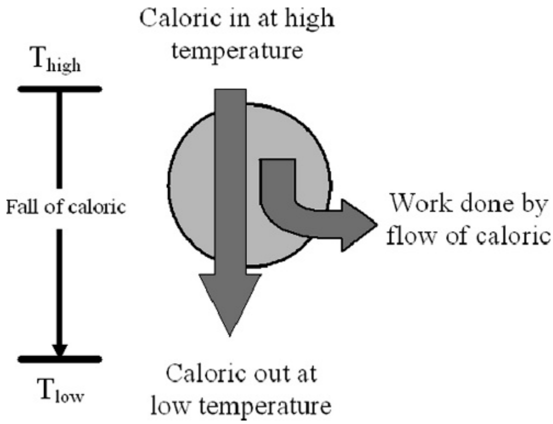

Fig. 1.1 Carnot's concept of flowing caloric. Work is done as caloric flows from a high temperature to a low temperature

is neither produced nor destroyed. It is true that it changes its form; that is it sometimes produces one kind of motion, sometimes another. But it is never annihilated." [[55], p. 30] We may easily substitute the modern term "energy" for "motive power." Then this is not only a rejection of the caloric theory, it is a clear, verbal statement of conservation of energy, which is the essence of the first law of thermodynamics.

1.3 The Laws

1.3.1 First Law

The relationship between heat and work is traditionally credited to the amateur scientist, James P. Joule,[6] in England. This is intermingled with the search for a conservation of energy, which occupied the attention of particularly German and English scientists in the 1840's [69, 75, 110, 128]. The difficulties were in part a consequence of the fact that the relationship between the commonly used term caloric and the developing concept of energy was not clear. That there was a relationship was evident. Hermann von Helmholtz[7] attempted to place the conservation of energy on firm grounds based on mechanics as well as the other sciences [69]. Von Helmholtz's arguments were visionary and based on a firm belief in a mechanical picture [[37] pp. 72–74].[8] But Joule performed the beautiful and critical experiments resulting in a laboratory measured result.

[6] James Prescott Joule (1818–1889).

[7] Hermann Ludwig Ferdinand von Helmholtz (1821–1894) was a German physician and physicist.

[8] The story is more nuanced. In 1847 von Helmholtz was a 26 year old physician. He finally had to arrange for a private publication after rejection by Poggendorff's Annalen.

Joule performed a series of experiments between 1840, when he was twenty one, and 1847. He was interested in equivalences among electrical, thermal, chemical, and mechanical effects. Many of the experiments he performed were technically very difficult. And his data often reflected the difficulty in the variation in results he obtained in the earlier experiments. In 1847 he began the series of experiments for which he is remembered, dealing with the relationship between mechanical work and heat.

It became quite clear to Joule that for the experiments he had planned a thermometer exceeding the accuracy of anything commercially available was necessary. He had thermometers capable of measurements of hundredths of a degree Fahrenheit made by J. B. Dancer, a Manchester instrument maker.

In Fig. 1.2 we illustrate the experiment for which Joule is famous. This is often simply called the Joule experiment, and we forget the previous six years of hard work.

In the experiment diagrammed in Fig. 1.2 Joule allowed a weight to fall through a measured distance. By the arrangement of a pair of pulleys this caused the shaft to turn and vertical vanes attached to the shaft churned the water in the vessel. The observed increase in temperature of the water in the vessel, which Joule measured with one of his specially constructed thermometers, was 0.563°F. This was a measurement of the heat transferred to the system.

Of course there was no heat actually transferred to the system because of the insulated vessel. An amount of work, proportional to the distance through which the weight fell, was done on the system. That was the point. Joule was interested in finding a mechanical equivalent of heat. In this experiment he obtained the value of $773.64\,\mathrm{ft\,lbf\,Btu^{-1}}$. The modern accepted value is $778\,\mathrm{ft\,lbf\,Btu^{-1}}$ [[37], p. 63].

Joule presented these results at the 1847 Oxford meeting of the British Association for the Advancement of Science, where he was asked to keep his presentation as brief as possible. After Joule's presentation there was silence until a young man stood up and pointed out the importance of what Joule had done. The young man

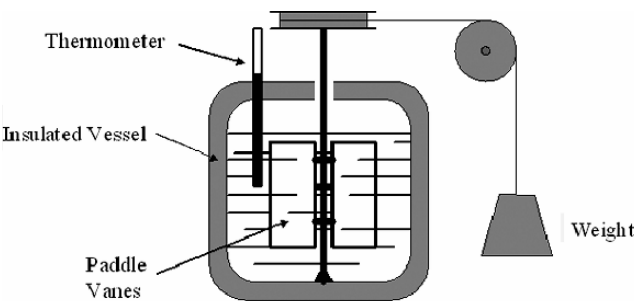

Fig. 1.2 One of the Joule experiments. The paddle wheels do work on the water in the insulated vessel as the weight falls. The thermometer measures the rise in temperature of the water

was Thomson,[9] who had just taken the position as professor of natural philosophy at Glasgow University, and would later become Lord Kelvin.

Thomson pointed out that in these experiments a certain amount of work was being done on an insulated system. For a given amount of work the result on the system, in this case the change in temperature, was always the same regardless of how the work was performed.[10] Doing work on an insulated system then produced a change in a property of the system, that is now called the internal energy.

The results of Joule's experiments may be taken as a statement of the first law [cf. [89], p. 152]. Heat is then introduced as a derived quantity. This approach has an attractive logic based entirely on experiment. We shall instead follow Rudolf Clausius' development, which introduces conservation of energy as a primary concept.

The first law of thermodynamics in its present form was published in 1850 by Clausius[11] [27] in Germany. But in 1850 Clausius referred to the internal energy as a "sensible heat." The confusion was resolved in 1865 with Clausius' great work on the second law [28–30], which was based on Carnot's work of 1824.

Clausius' ideas are represented in Fig. 1.3. In Fig. 1.3 the heat engine, is represented by a filled circle. The processes are cyclic. In (a) the heat Q_{in} entering the system from a high temperature source (reservoir) is separated into the heat Q_{out} flowing out of the system to a low temperature sink (reservoir) and the work done on the surroundings, W. The diagram (b) represents the reverse of (a). In (b) the heat taken in at the low temperature is combined with the work done on the system to produce an amount of heat transferred to the high temperature reservoir. This is possible if the heat engine is reversible, as Carnot required.

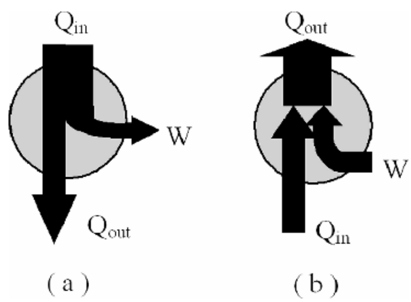

Fig. 1.3 Heat flow and work done in a cycle. Heat flow from high to low temperature can be made to produce work (**a**). Heat can be made to flow from low to high temperature if work is done on the system (**b**)

In Fig. 1.3 heat is not the conserved quantity. The total energy is conserved. The flow of this energy into the system is represented by Q_{in}. Part of this energy is converted into work W and part of it, Q_{out}, flows into the low temperature reservoir.

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9 William Thomson, 1st Baron Kelvin, OM, GCVO, PC, PRS, FRSE, (1824–1907) was a British mathematical physicist and engineer.

10 Some of Joule's experiments also measured heat produced by frictional processes.

11 Rudolf Julius Emanuel Clausius (1822–1888), was a German physicist and mathematician. Clausius formulated the second laws in terms of the entropy as a thermodynamic property. He was also instrumental in formulating atomic and kinetic theory of matter.

The amount of the heat which can be converted into work depends solely on the temperature difference.

Joule's equivalence of heat and work is evident in Fig. 1.3. But the engine is not insulated and there is no change in internal energy of the engine in a cycle. The cycle returns the engine, including the working substance contained in the engine, to its initial condition. There is then no change in any property of the engine. With the realization that energy is the conserved quantity we can combine Clausius' ideas in Fig. 1.3 with Thomson's interpretation of Joule's experiments.

Let us consider a small step in the cyclic process illustrated in Fig. 1.3. According to Thomson (and Joule) work done on an insulated system is equal to the increase in internal energy. According to Clausius, if the system is not insulated some of this internal energy is lost to the outside as an equivalent amount of heat.

During the small step in the cycle we are considering the engine is not insulated. Then the amount of work ΔW done on the system may initially give rise to a small increase in the internal energy ΔU of the system. But because the system is not insulated some of this internal energy is lost to the surroundings as an equivalent amount of heat ΔQ. That is, in the small step in the cycle

$$\Delta W\,(\text{on the system}) = \Delta U\,(\text{of the system}) + \Delta Q\,(\text{from the system})\,. \tag{1.1}$$

In utilizing heat to perform work we consider that heat is the source of the motion resulting in work done on the surroundings. Then we choose heat entering the system as positive and work done by the system as positive. Heat leaving the system and work done on the system are then negative and the terms ΔQ (from the system) and ΔW (on the system) in (1.1) are negative quantities. With this convention (1.1) becomes

$$\Delta Q = \Delta U + \Delta W. \tag{1.2}$$

Equation (1.2) is a general statement of a conservation of energy applied to a system in which only energy, but no mass, is transferred. The energy is transferred in the form of heat or work. The process generally results in a change in the internal energy of the system.

Of the three terms appearing in (1.2) only ΔU is the change in a system property and depends solely on the initial and final states of the process. The heat transferred and the work done depend upon the process. For example, we may choose to insulate the system in which case $\Delta Q = 0$. That is the first law for a closed system requires that the difference in two process dependent quantities, the heat transferred and work done, is always equal to a term which is dependent only on end states of the system.

1.3.2 Second Law

The second law is traditionally given verbally in terms that are expressed visually in Fig. 1.3. These statements were formulated by Thomson (Lord Kelvin) and Clausius.

The Kelvin statement of the second law denies the possibility of a cycle that converts all of the heat transferred to it into work. That is, the Kelvin statement denies the possibility of Fig. 1.3(a) with $Q_{\mathrm{out}} = 0$.

The Clausius statement of the second law denies the possibility of a cycle which transfers heat from a low to a high temperature reservoir without doing work on the system. That is, the Clausius statement denies the possibility of Fig. 1.3(b) with $W = 0$.

The second law does not deny Fig. 1.3(a) with $W = 0$. That is, heat flows naturally from high to low temperature without doing work. We may only transfer heat from a low to a high temperature in a cycle by performing work on the system during the cycle as shown in Fig. 1.3(b). The result is a refrigerator in which work is performed by the compressor.

There is nothing in the general statement of the first law that requires the process to run in one direction or the other. Energy is conserved whether we choose to obtain work from the flow of heat or to produce heat flow from work done. The second law, however, imposes a directionality. The natural flow of heat, when no work is done, is from high to low temperature.

The second law also imposes limitations on what we can do. Our engine has lost energy in the form of heat to a low temperature reservoir. In a sense this energy has been degraded. We can only use it in another cycle to obtain work if we have a still lower temperature to which we can exhaust heat. We have lost the possibility of using this low temperature energy in the same way that we used the energy stored in the reservoir at the high temperature.

If we allow a natural flow of heat from high to low temperature without producing useful work then we have lost an opportunity. This lost opportunity is irreversible.

In the 1865 paper Clausius [28] identified a new property, which he called the entropy from the Greek $\eta\tau\rho o\pi\eta$, which means transformation [[96], p. 80]. Entropy is a measure of irreversibility. In one of the great steps in theoretical physics, Clausius was able to show that entropy must increase whenever an irreversible process occurs in an isolated system. Specifically if any spontaneous process occurs inside the system, without any external cause, then there will be an increase in the entropy of the system. The entropy of Clausius is then a measure of the irreversible nature of a process occurring in a system.

Irreversible processes in a system may result from any of a number of causes. For example differences in temperature, electrical potential, concentrations will all result in irreversible motion of parts of a system. Such processes result in entropy increases, or entropy production within a system.

Clausius was able to obtain an expression for the infinitesimal change in the entropy of a closed system dS in a reversible process in terms of the infinitesimal amount of heat transferred reversibly during that process δQ_{rev} as

$$\mathrm{d}S = \frac{1}{T}\delta Q_{\mathrm{rev}}, \tag{1.3}$$

where T the thermodynamic temperature, which can never be zero. This mathematical definition may be used for the calculation of the change in the entropy. But

this definition is incomplete without the statement that the entropy must increase whenever an irreversible process occurs in the system.

The first and the second laws of thermodynamics are considered as the two great principles of the science. These were neatly tied together by J.W. Gibbs[12] at the end of the 19th century. We then possessed what was apparently a complete science of heat and motion. With that came the new discipline of physical chemistry.

Germany was particularly dependent on the chemical industry. And the next great step in thermodynamics came from Germany with roots in problems associated with the chemical industry. The third law was discovered by Walther Nernst[13] in Göttingen as he tried to resolve the problem of calculating equilibrium constants for reactions. The final formulation of the third law is in terms of the behavior of matter in the neighborhood of absolute zero of temperature. A consequence of the third law is the unattainability of absolute zero of temperature.

A specific reference value was required for the entropy in order to be able to calculate equilibrium constants for high temperature gas reactions. The third law provided this. In practical terms the third law has no effect on the Gibbs formulation. However, it has been indispensable for studies of chemical equilibrium and has motivated cryogenic studies (low temperature studies).

1.4 Modern Directions

Much of the more recent work in thermodynamics has been with nonequilibrium systems. This has resulted in no new laws, but has provided a deeper understanding of the second law. The behavior of nonequilibrium systems is based on the rate at which entropy is produced within the system. Particularly when coupled with the exploration of nonlinear dynamical systems and chaos, these ideas on entropy production provide great insight into some of the more fundamental questions related to the evolution of physical, chemical, and biological systems [49, 121, 133–135]. Such studies generally come under the blanket term of complexity or studies of complex systems. The term complexity has also found rather broad use outside of the scientific community. Nevertheless, it is one of the most active areas of interdisciplinary scientific study [122]. This is particularly because of the applications of these ideas in the neurosciences.

Modern work in thermodynamics also includes the application of statistical mechanics to nonequilibrium and to extreme conditions. Statistical mechanics cannot be separated from thermodynamics. It emerged logically from our attempts to understand the basic structure of matter and was motivated by an attempt to discover a microscopic (atomic and molecular) basis of the laws of thermodynamics. And the development of statistical mechanics engaged the same people who

[12] Josiah Willard Gibbs (1839–1903) was an American theoretical physicist, chemist, and mathematician. Gibbs was the first professor of Mathematical Physics at Yale College, now Yale University.

[13] Walther Hermann Nernst (1864–1941) was a German physicist.

were instrumental in the development of thermodynamics. particularly James Clerk Maxwell,[14] Clausius, and Gibbs.

These modern applications of statistical mechanics include studies of high temperature plasmas, such as those present in thermonuclear fusion devices such as the Tokamak, or encountered in astrophysics. Applications also include studies near absolute zero, where statistical mechanics provides an understanding of such phenomena as Bose-Einstein condensation (see Sect. 10.3.4).

1.5 Summary

In this chapter we have outlined the historical origins of the basic principles of thermodynamics in terms of the first, second, and third laws. The first law is a general statement of conservation of energy. We cannot produce something out of nothing. The second law denies us the possibility of using all of the energy we have. At every step we lose energy to a lower temperature. A result of the third law we cannot attain a temperature of absolute zero. Everything that we can imagine cannot always be accomplished.

In Chap. 2 we shall formulate these fundamental laws of thermodynamics in a way that makes them understandable in terms of the laboratory and in terms of application.

Exercises

1.1. In the textbook situation a scientific revolution occurs when there are two competing paradigms and one triumphs over the other. A paradigm is a pattern of thinking about some aspect of the universe. We saw that caloric appeared to be untenable but that there was no competing theory (paradigm). Try to think of another example, out of any branch of human knowledge, in which a paradigm shift has occurred based on the existence of competing theories. Try to think of an instance in which the first paradigm was not working, but there was no alternative.

1.2. Describe in your own words the points Carnot considered critical in developing a theory of the motive power of heat.

1.3. Figure 1.2 is a diagram of one of Joule's experiments. Design another experiment in which work can be used to heat water. Use your imagination, but recognize that your design must be possible.

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[14] James Clerk Maxwell (1831–1879) was a Scottish physicist. Maxwell is most remembered for his synthesis of electromagnetism. He was also a pioneer in the development of atomic physics and kinetic theory. Most of 19th century physics bears the imprint of Maxwell.

1.4. You want to carry out a Joule experiment to measure heat transfer in the nonadiabatic case. See Fig. 1.2. You construct two identical systems: one with an adiabatic boundary the other with a diathermal boundary. You arrange your pulley system so that you can drop the weights a large distance, i.e. out the window in a three storey building. For the adiabatic system you drop the mass, M, a height, H_0, and record a temperature change, ΔT. You notice that to get the same temperature rise in the diathermal case requires a distance, H, for the mass to fall.

(a) What is the heat transferred in the diathermal case?
(b) What assumptions have you made in the diathermal case? Consider the time.

1.5. A small explosion takes place inside a balloon with radius R and skin thick enough to remain in tact. The energy released in the explosion is $\mathscr{E}_{\mathrm{exp}}$. To a reasonable approximation the balloon skin can be assumed to be adiabatic and the pressure of the balloon skin on the gas inside P_b may be assumed constant. The explosion is sufficient to increase the balloon volume by 10%.
What is the change in the internal energy of the gas inside the balloon?

1.6. You have studied Carnot's ideas carefully and built a very efficient engine too. In each cycle your engine extracts an amount of heat Q_1 from a high temperature reservoir at the temperature T_1 and exhausts Q_2 to a low temperature reservoir at T_2. In each cycle your engine does a useful amount of work W. You can relate the heats transferred and the work done using the first law. Because you know the heats transferred and the (thermodynamic) temperatures you can also calculate the entropy changes ΔS_1 and ΔS_2 for the reservoirs. You obtain a relationship among the total entropy change $\Delta S_{\mathrm{T}} = \Delta S_1 + \Delta S_2$, the work done, and the heat input as $W = Q_1 (1 - T_2/T_1) - T_2 \Delta S_{\mathrm{T}}$ (show this). You then notice that your engine has a measured efficiency $\eta = (1 - T_2/T_1) - \varepsilon$ where ε is not very large. Using the definition of work done in terms of efficiency $W = \eta Q_1$ you find that $\varepsilon Q_1 = T_2 \Delta S_{\mathrm{T}}$ (show this). This intrigues you because it relates ε to ΔS_{T}. Comment on the result.

1.7. Place a wood cube at temperature T_1 on the wood laboratory table, which has a temperature $T_2 < T_1$. Neglect heat transfer from the cube to the room air. The heat transfer to or from a substance during a temperature change ΔT can be written as $C\Delta T$ where C is the heat capacity of the substance.

(a) What is the total entropy change in the laboratory during a (small) change in the cube temperature of ΔT?
(b) Is this entropy change positive or negative?
(c) You concluded in exercise 1.6 that positive entropy change means a loss. Does that concept hold here? Explain.

1.8. In Exercise 1.7 you found an expression for total increase in entropy during a temperature change ΔT. That is entropy increases when there is heat flow in

the presence of a temperature difference. Relate this finding to the third point in Carnot's memoire.

1.9. Without imposing an engine between high and low temperatures heat will naturally flow from the high to the low temperature. It will not reverse and flow the other way. Show that heat flow in the presence of a temperature gradient is then an irreversible process resulting in a positive production of entropy.

1.10. With the first law in the form (1.2) the change in system entropy can be written as $\mathrm{d}S = (\mathrm{d}U + \delta W)/T$ for a very small process. So we do not need to think of entropy as only related to heat transfer. Anything that changes internal energy or is related to work can change the entropy. And, provided our conclusions in the previous exercises are correct, irreversible processes will increase the entropy. What are some irreversible processes that can occur in a system that are candidates for producing entropy?

1.11. The entropy change of the sun is negative. The earth absorbs some of the energy from the sun at a much lower temperature. So entropy is absorbed by the earth. Where is the entropy coming from?